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(71)Applicant : ASAHI CHEM IND CO LTD

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(72)Inventor : NAKAO TAKU
INOUE YOSHIMITSU

(54) THERMOPLASTIC RESIN FOAM AND ITS PREPARATION

(57)Abstract:

PURPOSE: To obtain a thermoplastic resin foam having minute cells of a polyhedral structure which have substantially cell walls but are still interconnected by subjecting a thermoplastic resin blended with fine resin particles of a specific particle size to multi-stage blowing.

CONSTITUTION: This thermoplastic resin foam has a cell size of 1-20 μ m, a rate of cell wall existence of 80-100%, a rate of interconnected cells of 90-100%, and a density of 20-100kg/m³. A thermo-plastic resin blended with 0.05-5wt.% of fine resin particles having a particle size of 0.01-0.3 μ m is expanded by multi-stage blowing at a primary expansion ratio of 1.5-7. The thermoplastic resin is preferably a polycarbonate resin with its crystallinity controlled in the range of 0.1-5% carbon dioxide impregnation.

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CLAIMS

[Claim(s)]

[Claim 1] the diameter of air bubbles — 1-20 micrometers and cellular wall abundance — 80 - 100%, and the rate of an open cell — 90 - 100%, and a consistency — 20 - 100 kg/m³ it is -- thermoplastics foam characterized by things.

[Claim 2] The manufacture approach of the thermoplastics foam characterized by foaming to the thermoplastics which made the resin particle whose particle diameter is 0.01-0.3 micrometers blend 0.05 to 5% of the weight by one 1.5 to 7 times the primary expansion ratio of this by multistage foaming.

[Claim 3] The manufacture approach of thermoplastics foam according to claim 2 using the polycarbonate system resin adjusted as thermoplastics so that the crystallinity might become 0.1 - 5% according to carbon-dioxide-gas sinking in.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the foam used for the filler with which it is detailed air bubbles, and the air bubbles are used for the application of various filters, an adsorbent, etc. about the thermoplastics foam which is an open cell. When it uses as a filler for vacuum insulation material especially, it is related with the foam which has the description which can carry out [lightweight]-izing remarkably compared with the filler of the conventional inorganic system.

[0002]

[Description of the Prior Art] As an approach of conventionally obtaining the resin foam (or resin porous body) in which continuation micropore was formed ** Carry out phase separation of the system by cooling or the reaction after making homogeneity carry out dissolution mixing of resin and the solvent. the approach (JP,63-17904,A —) of obtaining a porous body by the so-called phase separation method for freezing if needed in the condition, extracting a solvent, and obtaining a porous body JP,4-50339,B etc. extrudes and carries out ** thermoplastics with a non-subtlety particle and a plasticizer. the approach (JP,58-32171,B —) of extracting a plasticizer and a non-subtlety particle and obtaining a porosity sheet, a hollow filament, etc. after obtaining the shape of a sheet, and a fibrous object the approach (JP,44-30753,B —) of obtaining the porous body of the shape of sponge, such as polyurethane resin of ** reaction hardening molds, such as JP,60-23130,B JP,61-51021,A, JP,4-63845,A, etc., ** After fusing olefin system resin etc. with an extruder and pouring in a foaming agent further, The methods (JP,63-309535,A, JP,4-170443,A, JP,5-23297,B, etc.) of applying the so-called extrusion-foaming technique made to decompress and foam, and obtaining open-cell foam are learned. however, the resin frame part in which the approach of ** is equivalent to the diameter of air bubbles of foam — homogeneity about several micrometers or less — although a detailed continuation hole is obtained — the hole — a configuration has few parts equivalent to a cellular wall, and it only passes over resin only to extent which is making the stanchion of a porous body frame. Moreover, the resin part was deposited after phase separation out of the solution, it was formed, and there was no improvement contribution in on the strength by extension orientation etc., the reinforcement as this kind of the whole low consistency porous body was weak, and, for that reason, that application was restricted. ** Although the detailed continuation hole was formed by the approach and it was strong in reinforcement, it was difficult to obtain the thing and the thing of a low consistency of the shape of a thick sheet. ** It was little continuation pore of the rate of the part which is equivalent to a cellular wall in a configuration similar to ** by the approach, even if it moreover made the pore diameter small, it was about at most 60-70 micrometers, and various things for which the pore diameter is made small were technically difficult although it inquired. ** Although the approach was continuously producible, even if the diameter of air bubbles was small, it was about at most 200 micrometers, and it was technically difficult to make the diameter of air bubbles small.

[0003] As mentioned above, although various approaches had been examined, in the foam which has an open cell, the diameter of air bubbles, the cellular configuration, and the foam consistency

had the limit for which it comes from the process, respectively by the Prior art. The resin foam of a low consistency which serves as free passage air bubbles while it has the detailed cellular structure of 20 micrometers or less of diameters of air bubbles also especially in it and the cellular wall had moreover been made to remain substantially was what must have been attained.

[0004] The detailed air-bubbles resin foam which realizes lightweight-ization in the range on which reinforcement is not dropped for the purpose of reducing the amount of the thermoplastics used on the other hand is examined, and the attempt which makes the diameter of foam air bubbles small has been examined variously. For example, U.S. Pat. No. 4473665 and Polymer Although the process of the resin foam of detailed air bubbles is indicated by Eng.Sc., 27, P485-492, and ANTEC'91.P1406 - 1410 grade considering the purpose — each — a closed cell — and expansion ratio — 2 to 3 times (even if high about at most 10 times) as many foam as this — it is — the open cell of this invention — and the place clearly made into the aim differed from the resin foam of a low consistency (high twice foaming).

[0005]

[Problem(s) to be Solved by the Invention] This invention makes a technical problem the low consistency resin foam which is an open cell with the conventional technique, having the detailed air bubbles of the polyhedron structure which is the so-called fundamental air-bubbles configuration of the resin foam which was not able to be attained, and having the cellular wall substantially.

[0006]

[Means for Solving the Problem] In order to solve said technical problem, as a result of inquiring wholeheartedly about the detailed open cell [having had the cellular film substantially / are detailed air bubbles and] resin foam which was not examined at all conventionally, it came to complete this invention. namely, the thermoplastics foam of this invention — the diameter of air bubbles — 1-20 micrometers and cellular wall abundance — 80 - 100%, and the rate of an open cell — 90 - 100%, a consistency 20 - 100 kg/m³ it is — it is thermoplastics foam characterized by things.

[0007] Moreover, the manufacture approach of this invention is the manufacture approach of the thermoplastics foam characterized by foaming to the thermoplastics which made the resin particle whose particle diameter is 0.01-0.3 micrometers blend 0.05 to 5% of the weight by one 1.5 to 7 times the primary expansion ratio of this by multistage foaming. Hereafter, the contents are explained. The foam of this invention is foam which consists of air bubbles which have a cellular wall substantially, and the surface part ***** air-bubbles wall of polyhedron configuration air bubbles is foam characterized by air bubbles having free-passage-ized by having the deficit section represented in the hole through which matter, such as a gas and a liquid, may pass in a part of the cellular wall, a gash, etc., had.

[0008] The air bubbles and the cellular wall in this invention correspond to the definition of the cel and cel face which are specified with books "the activity of a cellular structure object and a porous material sake" (L. J.Gibson, M.F.Ashby work, a Masahisa Otsuka translation, Uchida Rokakuho Publishing Publishing office) respectively. A cel is the minute space of a polyhedron configuration with ** (edge) and a field (face), and, specifically, a cel face is a part defined by the field (face) surrounding a cel.

[0009] The diameter of air bubbles of the foam of this invention needs to be in the range of 1-20 micrometers. Here, the diameter of air bubbles of foam is the value which observed the cross section of foam and was calculated on the average based on ASTM-D-3576 with the electron microscope photograph of an about 100 to 1000-time scale factor. When it uses as the description as detailed air bubbles, for example, a bulking agent for vacuum insulation, it is whenever [reduced pressure / of 10 to 1 or more mmHg], and in order to demonstrate the engine performance, it is necessary to be 20 micrometers or less. Moreover, since it becomes difficult to obtain the thing of a low consistency (it is difficult to make it quantity-double-foam), the thing of the less than 1-micrometer diameter of air bubbles is restricted. 2-15 micrometers of 3-10 micrometers of diameters of air bubbles are 4-8 micrometers still more preferably more preferably.

[0010] The cellular wall abundance of the foam of this invention needs to be in 80 - 100% of range. It specifically asks for the cellular wall abundance of foam with the following measuring methods. First, the existence of the deficit section of a cellular wall and its configuration select at least 20 or more air bubbles which can fully be observed from the enlargement (it observes for the scale factor for which at least 100 or more air bubbles are observed.) of the arbitration cross section of foam obtained by scanning electron microscope observation etc. Next, image-analysis equipment etc. is used, and it asks for that total (this value is set to A), after asking for each cross section of the selected air bubbles. About the air bubbles which furthermore have the deficit section, it asks for that total (this value is set to B), after asking for that each aspect product (area when projecting a deficit part at right angles to a cross section so that it can measure on a photograph) of a deficit with image-analysis equipment etc. similarly. Here, with cellular wall abundance, the value (%) acquired by $\{1-(B/A)\} \times 100$ is adopted. A micro crack with observation difficult as that in which cellular wall abundance has area with a scanning electron microscope in 100% of thing here exists in a cellular wall, and is considered that air bubbles are open for free passage. Especially as for the foam characterized by the structure of having 80% or more of cellular wall of this invention, it is the greatest description that compressive strength is high in part since the cellular wall with which the deficit section was extended at the time of foaming of a certain thing exists in the cellular wall substantially. Since, as for less than 80% of thing, the compressive strength as foam tends to fall, cellular wall abundance is restricted. Cellular wall abundance is 98 - 100% of range still more preferably 95 to 100% more preferably 90 to 100%. The place which should be emphasized again here the cellular configuration of the foam of this invention The resin solid-state part which is the characteristic structure of the polyurethane system foam which has an open cell, and the porous body formed by the above-mentioned phase separation method is the arris part (the edge part which borders a cel face is meant as it defines as the above-mentioned reference book family register. cel edge:) of a polyhedron. The condensed structure is the point that the cellular configurations differ greatly, like a long and slender linear stanchion.

[0011] The rate of an open cell of the foam of this invention needs to be in 90 - 100% of range. When it uses as the description as an open cell, for example, a filler for vacuum insulation, it is necessary to be 90 - 100% because of prevention of a fall whenever [by compaction of vacuum reduced pressure time amount, and diffusion of the air from the closed cell section / reduced pressure]. This rate of an open cell is the value computed from the rate of a closed cell for which it asked based on ASTM D-2856. However, when it is foam in which the non-foamed layer on the front face of foam and the so-called skin were formed, the value in removal or the real busy condition after destroying in part is adopted for a skin. The approach of slicing and removing a skin part mechanically as an approach of removing or destroying a skin, the approach of forming a hole or a slot in a skin, the approach that make foam breaking easy to plasticize a skin with an additive and to carry out, or the approach heat concentrates with an additive at the time of foaming heating, and it is made to generate heat is chosen suitably, and it gets. The rate of an open cell is 99 - 100% still more preferably 97 to 100% more preferably 95 to 100%.

[0012] the foam consistency of the foam of this invention — 20 - 100 kg/m³ it is necessary to be . Consistencies are 20 kg/m³. For the thing of the following, since it is the inclination for foam reinforcement to become weak, it is restricted, and consistencies are 100 kg/m³. Since the inclination of the degree of lightweight-izing becomes small, what is exceeded is restricted. the foam consistency of this invention — desirable — 30 - 80 kg/m³ — more — desirable — 35 - 70 kg/m³ — further — desirable — 40 - 60 kg/m³ It is the range. This foam consistency is the value calculated based on JISK-6767.

[0013] As thermoplastics used for the foam of this invention Common well-known polycarbonate system resin, polymethacrylate system resin, polystyrene system resin, Polyphenylene ether system resin, polyarylate system resin, polysulfone system resin, Amorphous thermoplastics, such as polyether sulfone system resin and polyether imide system resin, Crystalline thermoplastics, such as polyethylene terephthalate system resin, polyphenylene sulfide system resin, polyamide system resin, a polypropylene resin, polyethylene system resin, and polyoxymethylene system resin, can use suitably in combination with the optimal foaming agent.

Preferably, the so-called hard thermoplastics whose glass transition point of thermoplastics is beyond a room temperature is used from the holdout of the compressive strength in a room temperature. Also in it, especially the hard thermoplastics of amorphism nature has the description which detailed air-bubbles formation tends to carry out. They are polycarbonate system resin, polymethacrylate system resin, polystyrene system resin, and polyphenylene ether system resin still more preferably. They are the polycarbonate system resin which contains the so-called bisphenol A in a principal chain, and polymethacrylate system resin which contains methyl methacrylate in a principal chain especially preferably.

[0014] Although it can use independently, these resin may be blended and used in order to improve the resin melt viscosity in the heating condition at the time of foaming, and the holdout of a foaming agent. Additives, such as well-known lubricant, a thermostabilizer, and an ultraviolet ray absorbent, may be added and used in the range which does not change fizz to 1 pan remarkably if needed. Next, the manufacture approach of this invention is explained.

[0015] In order to manufacture the foam of this invention, it is important to combine the formula which makes homogeneity generate remarkable detailed air bubbles compared with usual foam, and the formula which makes the detailed air bubbles made to generate open-cell-ize in early stages of foaming. The method of sinking in and heating the high-pressure carbon dioxide gas in a gaseous-phase condition, a liquid phase condition, and a supercritical condition, nitrogen gas, oxygen gas, air, etc. to the thermoplastics which put in the physical foaming agent into the high pressure vessel as a formula which generates detailed air bubbles to homogeneity in the so-called sinking-in foaming into which resin was infiltrated, and which carries out a late-coming bubble under high pressure in consideration of temperature and time amount, and making it generate detailed air bubbles can take. In extrusion foaming, high-pressure carbon dioxide gas, nitrogen gas, oxygen gas, air, etc. are poured into the resin fused within the extruder, and the approach of adjusting resin viscosity more highly and carrying out open aggressiveness foaming at a dice outlet can take. Moreover, as a formula which makes the detailed air bubbles made to generate open-cell-ize, the approach of promoting foam breaking (a cellular wall being open cell-ization by the defective-part formation by destruction a part) can take by sinking-in foaming by investigating the relation of the foaming temperature and the expansion ratio which are the foaming conditions after sinking in, and heating at the temperature which shows the peak of the expansion ratio of resin. However, the approach for which it was suitable especially as an approach of obtaining the foam of this invention is the manufacture approach of this invention shown below. Hereafter, the contents are explained.

[0016] The manufacture approach of this invention is the manufacture approach of the thermoplastics foam characterized by foaming to the thermoplastics which made the resin particle whose particle diameter is 0.01–0.3 micrometers blend 0.05 to 5% of the weight by one 1.5 to 7 times the primary expansion ratio of this by multistage foaming. It describes from the formula which makes detailed air bubbles generate first. adding non-subtlety particles, such as talc, a silica, and a magnesium oxide, and using it as a foaming nucleating agent at the time of foaming by extrusion foaming, conventionally, inquires — having had (for example, J.Appl.Polym.Sci., 28, 1983 grades) — at most, even if the diameter of air bubbles was small, it was about 200 micrometers. The detailed air-bubbles resin foam which used HIPS (high-impact-polystyrene resin) for reference (ANTEC.'92.P1078-1081, ANTEC.'93.P1828-1831) in order to make the diameter of air bubbles small furthermore is indicated. The resin which blended the butadiene system rubber particle in polystyrene resin is known in order to improve the shock resistance of polystyrene generally. Although magnitude, its amount of blends, etc. of a rubber particle were examined variously, for shock-proof amelioration, the diameter of a rubber particle was made suitable [that whose amount of blends is 10 – 30 % of the weight], and, as for these, came by about 1–2.5 micrometers. It is presumed that that serves as a foaming nucleus since a micro void occurs in the rubber particle of the diameter of an average of 2 micrometer with the thermal stress generated by this reference when the coefficients of thermal expansion of a polybutadiene-resin part and polystyrene resin differ in HIPS. A particle consistency and a cellular consistency (a cellular consistency is surveyed from the cross-section microphotography of foam) the number of air bubbles per foam unit volume — an individual /

cm³, so that expansion ratio is so high that it expresses in a unit and the diameter of air bubbles is small — more — a cellular consistency — high — becoming — 108 –1010 piece/cm³ in the range, it is proportional — Moreover, since some whose diameter of a polybutadiene particle is 2 micrometers have the effectiveness as a foaming nucleus, what is 0.025 micrometers is too small and the effectiveness does not exist, although it is not in **, it is also indicated that the diameter of criticality of the diameter of a particle which contributes effectively exists. However, although there is no publication about expansion ratio, it is presumed that it is low expansion ratio compared with this invention. for making expansion ratio high in order to be in level (it is the range of 3 1010–1013 pieces/cm when it says by the cellular consistency) still higher than the cellular consistency indicated by this reference by this invention and to make it a low consistency moreover, it is necessary to improve holdout of the foaming agent in air bubbles — in addition, the thing of making a cellular wall tear and open-cell-ize done for phase conflict must be made to attain By the system which blended 2 micrometers of diameters of a particle of the publication proved by reference, it is impossible. That is, if the particle which exists in a cellular wall is too large, before a cellular wall will reach need expansion ratio, foam breaking is carried out, if a particle is too small, it cannot become an effective foaming nucleus, or a cellular wall will not be made to generate a micro crack, but extent of the formation of free passage air bubbles will become low. However, a certain amount of difference may generate the behavior in the cellular wall of this particle with the rate of the deformation which followed in footsteps of the cellular wall by plasticization extent of the particle by the foaming agent, or the change rate of the viscoelasticity in foaming temperature. While advancing this invention based on such an operation result, the conditions whose detailed foaming is enabled were found out in a different field from what was examined by the conventional shock-proof amelioration about the diameter of a rubber particle, and its amount of blends. It is thought that this effectiveness has contributed to micro crack generation of a cellular wall to think because for resin and a particle interface to serve as a foaming nucleus in early stages of foaming, and also for this interface consider as an open cell finally. Specifically, detailed foaming was attained by blending a resin particle with a particle diameter of 0.01–0.3 micrometers 0.05 to 5% of the weight to thermoplastics. A resin particle here may be a globular form particle by which a polymerization is carried out by the general well-known emulsion polymerization, the seed polymerization, the distributed polymerization, a suspension-polymerization method, etc., and may be a particle which has a core shell mold and multilayer structure in consideration of particle dispersibility, the foaming agent dispersibility after sinking in, etc. Preferably, a multilayer-structure acrylic (polymethylmethacrylate) rubber system particle, a styrene-butadiene system rubber particle, an acrylonitrile-styrene-butadiene system particle, a silicon system particle, a polystyrene particle, a polymethylmethacrylate particle, etc. are used. It cannot become a foaming nucleus, and if too small, if too large, open cell-ization will take place in early stages, and since it is in the inclination for expansion ratio to become low, the diameter of a particle is restricted. The range of 0.05–0.2 micrometers of diameters of a particle is 0.07–0.15 micrometers still more preferably preferably. The diameter of a particle here adopts the value which averaged the electron microscope etc. from observation and was calculated. if there are still too few amounts of blends of a particle — a foaming nuclear number — being few (the diameter of air bubbles becoming large) — moreover, if many [too], open cell-ization will take place in early stages, and since it is in the inclination for expansion ratio to become low, it is restricted. The amount of blends is 0.07 – 0.5 % of the weight still more preferably 0.05 to 1% of the weight preferably. A well-known compatibilizer etc. may be used together if needed [of improving dispersibility and the adhesive property of an interface].

[0017] Although it furthermore adds and is crystallinity originally [, such as polycarbonate resin and polyethylene terephthalate resin,] as this formula, when making it foam, by the resin which can take amorphous state by the quenching processing at the time of processing etc., very detailed air bubbles can be formed by making the microcrystal generate. For example, the processing which can form a microcrystal is suitably chosen at the time of foaming agent sinking in with plasticizing capacity, such as heat treatment and solvent processing before foaming agent sinking in, and/or carbon dioxide gas. What was immersed in the aliphatic series system

hydrocarbon system partially aromatic solvent included a 15 capacity % grade in the acetone, specifically carried out solvent processing of the polycarbonate resin, sank in and foamed to carbon dioxide gas after that serves as foam which has very detailed air bubbles. In addition to solvent processing, by having carried out carbon-dioxide-gas sinking in, a microcrystal (less than 5% has the desirable degree of crystallinity by temperature up conditions by DSC:10-degree-C/) generates to homogeneity in polycarbonate resin, it serves as a foaming nucleus, and this is considered to be the effectiveness by the cellular nuclear number having increased remarkably. Moreover, it is desirable to adjust degree of crystallinity to 0.1% or more in that the effectiveness of having made the microcrystal which can serve as a foaming nucleus generating is demonstrated.

[0018] Next, the detailed air bubbles made to generate are described about the formula made to open-cell-ize. As an approach to which the resin adjusted like the above is made to foam in the manufacture approach of this invention Although the so-called extrusion foaming to which release ** and it is made to foam can be suitably chosen after pressing a foaming agent fit in the resin which fused the physical foaming agent within the so-called sinking-in foaming into which resin is infiltrated, and an extruder under high pressure and mixing to homogeneity In any case, when foaming and foam breaking (a cellular wall is open cell-ization by the deficit section formation by destruction a part) cannot be satisfied with coincidence of the physical properties of the foam of this invention at the time of one step of usual foaming, it is very effective to perform multistage foaming of sinking in and foaming to a physical foaming agent again at the obtained foam. this holding down the first step of foaming to one 1.5 to 7 times the expansion ratio of this for the purpose of forming many foaming nuclei, and raising further the mind bubble pressure inside the air bubbles formed in the foam formed by primary foaming after the second step of foaming — it is — the high twice of expansion ratio — it is a formula aiming at-izing and foam breaking. It cannot be overemphasized that the method of foaming multistage [three or more steps of] for performing sinking in and foaming further can be taken if needed. that, as for what there is an inclination which air bubbles generate [primary expansion ratio] to an ununiformity by less than 1.5 times, and exceeds 7 times, the diameter of air bubbles increases by coalescence of air bubbles in the phase, and foam breaking — foaming quantity twice — since there is an inclination for-izing to become difficult, it is restricted. It is 2.5 to 5 times the primary expansion ratio of this more preferably two to 6 times. The amount of sinking in of the physical foaming agent used by primary sinking in can be suitably chosen in the range of 6 – 40 weight section, taking into consideration a foam consistency, i.e., expansion ratio. desirable — 8 – 30 weight section — it is 10 – 24 weight section more preferably.

[0019] The solvent system foaming agent, organic, and the inorganic system gas foaming agent which are used for general well-known foam as a physical foaming agent used by this invention are chosen suitably, and it gets. Specifically Normal butane, an isobutane, a normal pentane, a cyclopentane, Aromatic hydrocarbon, such as aliphatic hydrocarbon, such as normal hexane, benzene, toluene, and a xylene, Ketone system hydrocarbons, such as an acetone and a methyl ethyl ketone, a methanol, Alcoholic system hydrocarbons, such as ethanol, dihydrodifluoromethane, pentafluoro ethane, It is inorganic gas, such as fluorine-containing hydrocarbons, such as 1, 1, 2, and 2-tetrafluoro ethane, 1, 1 and 1, 2-tetrafluoro ethane, 1 and 1, 1-trifluoro ethane, 1, and 1-difluoroethane, 1, and 2-difluoroethane, carbon dioxide gas, and nitrogen gas, oxygen gas, etc. Especially in order to make it small making [many / as possible] the cellular nuclear number per foam unit volume of air bubbles, i.e., the diameter in fixed expansion ratio, carbon dioxide gas is desirable. Moreover, other physical foaming agents may be used together or ***** (ed) to carbon dioxide gas for the purpose which increases the cellular nuclear number at the time of foaming. The amount of sinking in of a foaming agent is usually 3 – 25 weight ***** , although it is suitably chosen with the physical foaming agent to be used and being got. desirable — 5 – 20 weight section — it is 7 – 15 weight section more preferably.

[0020] As a physical foaming agent which sinks into foaming after secondary again, in consideration of primary expansion ratio, plasticization extent by sinking in, the foaming temperature after secondary, expansion ratio, the rate of open-cell-izing, etc., it is suitably

chosen from the below-mentioned physical foaming agents, and gets. if it is not made to foam, carrying out foam breaking of the cellular wall of the closed cell formed by foaming in the preceding paragraph at the time of foaming after secondary, it is necessary to make gas pressure in air bubbles into height, and while the amount of sinking in of a foaming agent takes into consideration a foam consistency, i.e., expansion ratio, in the range which fulfills the condition, for a 7 ** reason, it can choose suitably in the range of 6 - 40 weight section. desirable — 8 - 30 weight section — it is 10 - 24 weight section more preferably.

[0021] The physical foaming agent which can be used by this invention is introduced in high pressure vessels, such as an autoclave into which a well-known approach, for example, the bead of thermoplastics, powder, a pellet, a sheet-like object, etc. were put, and it sinks in under high-pressure conditions. Sinking-in conditions and the amount of sinking in are suitably chosen in consideration of the expansion ratio and foaming temperature which are needed, and it deals in them. Moreover, in the case of extrusion foaming, a sinking-in condition can be chosen as the fused resin for a physical foaming agent by the distributed mixing **** technique. Moreover, when making the thing of the shape of a bead of the thermoplastics in which it is produced by the suspension polymerization and deals foam, a physical foaming agent can be added in the second half of the suspension polymerization, and an expandable bead can also be obtained.

[0022] As a heating means at the time of foaming, hot blast heating which is a well-known approach, heating oil heating, far infrared heating, steam heating also including primary foaming and subsequent multistage foaming, etc. are chosen suitably. When especially the resin with comparatively high steam permeability, such as styrene resin and polycarbonate resin, carries out steam heating, using the property effectively, quantity twice foam is obtained.

[0023] It is also the description that the foam of this invention is obtained in a process with the simple thing of the configuration of arbitration to the foam of particle shape which is represented by styrene system bead foam, and the foam of a sheet configuration.

[0024]

[Example] Hereafter, this invention is explained to a detail using an example.

[0025]

[Example 1] By the approach given in JP,3-68627,A, melting extrusion was performed for the pellet of the polycarbonate resin (weight average molecular weight 56,000) manufactured from diphenyl carbonate and 2 and 2-screw (4-hydroxyphenyl) propane at 320 degrees C of cylinder temperatures using the extruder, and the sheet with a thickness of 1mm was created.

[0026] A 20x30mm sample is started from this sheet, and it puts into a small autoclave, and is a liquefied carbon dioxide at 5 degrees C 40kg/cm² It pressed fit and was left for 24 hours so that it might become. Then, when ** was released and the weight of a sample was measured, the 13.5 weight sections and carbon dioxide gas sank in to sample weight. When it was immersed in the oil bath with a temperature of 150 degrees C for 30 seconds, and this sinking-in sample was heated to it and made to foam to it primarily, foam 4.8 times the scale factor of this was obtained.

[0027] this primary foaming article — again — a small autoclave — putting in — the same — carbon dioxide gas — 60kg/cm² up to — it pressed fit and was left at 23 degrees C for 24 hours. Then, it was left at 23 degrees C to the condition that release ** and 15 weight sections carbon dioxide gas sinks in to sample weight. When it was immersed in the oil bath with a temperature of 190 degrees C for 15 seconds, and this sinking-in sample was heated to it and made it to carry out post expansion, it is consistency 57 kg/m³. Foam of 7 micrometers of diameters of air bubbles was obtained.

[0028] The cellular wall abundance which searched for the 1000 times as many electron micrograph as this foam cross section with image-processing analysis equipment (SPICCA-II by Nippon Avionics [Co., Ltd.] Co., Ltd. is used) was 98%, and the rate of an open cell of foam (the sample was quadrisected and measured in order to remove the effect of a skin) was 99%. Therefore, although almost all air bubbles were open cells, it turned out that it has the cellular wall substantially.

[0029]

[Examples 2-5] Examples 2-4 manufactured foam on the conditions which an example 5 is the same approach as an example 1 using the polycarbonate resin (Teijin Formation bread-making

light K-1300) of weight average molecular weight 30,000, and show the same resin as an example 1 in Table 1. The physical properties of the obtained foam are shown in Table 1.

[0030]

[Example 6] After carrying out the dryblend of the acrylic particle (acrylic rubber SRS by Asahi Chemical Industry Co., Ltd.: particle diameter of 0.1 micrometers) to polymethylmethacrylate resin (DERUPETTO by Asahi Chemical Industry Co., Ltd. 980N) at 0.1% of the weight of a rate, with the geared type said direction twin screw extruder, water-cooled desiccation was carried out after extrusion at 250 degrees C, and the melting blend pellet was obtained. Press forming of this blend pellet was carried out, and the sheet with a thickness of 1mm was obtained. When the 20x30mm sample was started from this sheet, it put into the small autoclave and 80 degrees C sank in over 60 hours by HFC134a (1, 1, 1, 2-tetrafluoro ethane) of a liquid phase condition, the amount of sinking in was 25 weight sections. It was immersed in the 150-degree C silicon oil bath for 30 seconds, and foamed to this sinking-in sample, and the primary foaming article 6.5 times the expansion ratio of this was obtained. When this sample was again put into the autoclave and 30 degrees C sank in over 48 hours by HFC134a of a gaseous-phase condition, the amount of sinking in was 35 weight sections. This sinking-in sample was immersed in the 150-degree C silicon oil bath for 30 seconds, and the post expansion object was acquired. the diameter of air bubbles of this foam — 3 micrometers and cellular wall abundance — 95% and the rate of an open cell — 95% and a consistency — 70kg/m3 it was .

[0031]

[Example 7] The 30x20mm sample was started from the same sheet as an example 1, it was immersed in the mixed solution of acetone:n pentane =20:80 (capacity factor) at the room temperature for 24 hours, and the solvent processing sheet containing 10 weight sections partially aromatic solvent was obtained. this sheet — a small autoclave — putting in — carbon dioxide gas — 40kg/cm2 up to — it pressed fit and was left at 5 degrees C for 24 hours. Then, when ** was released and the weight of a sample was measured, 20 weight sections, carbon dioxide gas, and a solvent sank in to sample weight. the part which was not observed with the sheet before sinking in in a part of this sinking-in sample although it was 3% or less when that degree of crystallinity was measured in DSC — crystallization was seen.

[0032] When it was immersed in the oil bath with a temperature of 150 degrees C for 30 seconds, and this sinking-in sample was heated to it and made to foam to it primarily, foam 3.0 times the expansion ratio of this was obtained. this primary foaming article — again — a small autoclave — putting in — the same — carbon dioxide gas — 40kg/cm2 up to — it pressed fit and was left at the room temperature for 24 hours. ***** was released, it aged at the room temperature, and 13 weight sections carbon dioxide gas changed into the condition of sinking in, to sample weight.

[0033] When it is immersed in an oil bath with a temperature of 190 degrees C for 15 seconds, and this sinking-in sample is heated to it and made it to carry out post expansion, the diameter of air bubbles is [99% and the rate of an open cell of 5 micrometers and cellular wall abundance] 90%, and consistencies are 50 kg/m3. Foam was obtained. Compared with an example 1, a foaming nucleus increases this foam by solvent processing, and the diameter of air bubbles is considered to have become small.

[0034]

[The example 1 of a comparison] With the oil bath with a temperature of 190 degrees C, it was immersed for 30 seconds, the primary sinking-in sample obtained on the same conditions as an example 1 using the same resin as an example 1 was heated, and foam was obtained. the diameter of air bubbles of the obtained foam — 9 micrometers and cellular wall abundance — 99% and a consistency — 45 kg/m3 it was — although — the rate of an open cell was a low value compared with 57% and an example.

[0035]

[The example 2 of a comparison] The mixed solvent (70:30 capacity %) of 10 weight sections, and a dioxane/cyclohexane was heated at 60 degrees C on ***** which becomes a depth of about 1cm about 90 weight sections at a metal cylinder container with a diameter of 50cm, and an oil bath, and the same polycarbonate resin as an example 5 was dissolved in homogeneity. It was

rapidly immersed in the dry ice bus, this container was quenched below to solidification temperature, and resin porosity intermediate field were obtained. While the vesicular structure had been made to hold this intermediate field using a freeze dryer, the solvent was removed, and the resin porous body was obtained. the diameter of air bubbles of this resin porous body (path of the part equivalent to the diameter of air bubbles in foam) — 5 micrometers — it is — cellular wall abundance — 0% — it is — the rate of an open cell — 100% and a consistency — 115 kg/m³ it was . This resin porous body did not have a cellular wall substantially so that cellular wall abundance might show, and that compressive strength was remarkably low compared with the foam of this invention.

[0036]

[Table 1]

(単位)	実 施 例							比 較 例	
	1	2	3	4	5	6	7	1	2
熱可塑性樹脂	PC	PC	PC	PC	PC	PMMA	PC	PC	PC
一次含浸									
・発泡剤	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	134a	CO ₂	CO ₂	
・含浸温度 (°C)	5	5	5	5	5	80	5	5	
・含浸圧力 (kg/m ²)	40	40	40	40	40	24	40	40	
・含浸時間 (時間)	24	24	24	24	24	60	24	24	
・含浸量 (重量部)	13.5	11.5	10.5	12.5	13.0	25	20	13.5	相分離法
一次発泡									
・加熱温度 (°C)	150	150	155	155	150	150	150	190	
・加熱時間 (時間)	30	30	30	30	30	30	30	30	
・発泡倍率 (倍)	4.8	3.4	5.5	5.0	3.3	6.5	3.0	26.0	
二次含浸条件									
・発泡剤	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	134a	CO ₂		
・含浸温度 (°C)	23	5	5	23	23	30	5		
・含浸圧力 (kg/m ²)	60	40	40	60	60	48	40		
・含浸時間 (時間)	24	24	24	24	24				
・含浸量 (重量部)	15.0	18.0	8.5	12.5	13.0	34.5	13.0	—	—
二次発泡									
・加熱温度 (°C)	190	190	190	190	185	150	190		
・加熱時間 (時間)	15	15	10	20	15	30	15		
発泡体物性									
・気泡径 (μm)	7	8	15	10	20	3	4	9	5
・気泡壁存在率 (%)	98	98	90	98	95	95	99	99	0
・連続気泡率 (%)	99	99	99	100	100	95	96	57	100
・密度 (kg/m ³)	57	40	95	31	24	70	50	45	115

[0037]

[Effect of the Invention] The thermoplastics foam of this invention is low consistency foam which formed continuation detailed air bubbles in homogeneity, and since the air bubbles moreover have the cellular wall substantially, it is excellent in reinforcement.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the foam used for the filler with which it is detailed air bubbles, and the air bubbles are used for the application of various filters, an adsorbent, etc. about the thermoplastics foam which is an open cell. When it uses as a filler for vacuum insulation material especially, it is related with the foam which has the description which can carry out [lightweight]-izing remarkably compared with the filler of the conventional inorganic system.

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PRIOR ART

[Description of the Prior Art] As an approach of conventionally obtaining the resin foam (or resin porous body) in which continuation micropore was formed ** Carry out phase separation of the system by cooling or the reaction after making homogeneity carry out dissolution mixing of resin and the solvent. the approach (JP,63-17904,A ---) of obtaining a porous body by the so-called phase separation method for freezing if needed in the condition, extracting a solvent, and obtaining a porous body JP,4-50339,B etc. extrudes and carries out ** thermoplastics with a non-subtlety particle and a plasticizer. the approach (JP,58-32171,B ---) of extracting a plasticizer and a non-subtlety particle and obtaining a porosity sheet, a hollow filament, etc. after obtaining the shape of a sheet, and a fibrous object the approach (JP,44-30753,B ---) of obtaining the porous body of the shape of sponge, such as polyurethane resin of ** reaction hardening molds, such as JP,60-23130,B JP,61-51021,A, JP,4-63845,A, etc., ** After fusing olefin system resin etc. with an extruder and pouring in a foaming agent further, The methods (JP,63-309535,A, JP,4-170443,A, JP,5-23297,B, etc.) of applying the so-called extrusion-foaming technique made to decompress and foam, and obtaining open-cell foam are learned. however, the resin frame part in which the approach of ** is equivalent to the diameter of air bubbles of foam --- homogeneity about several micrometers or less --- although a detailed continuation hole is obtained --- the hole --- a configuration has few parts equivalent to a cellular wall, and it only passes over resin only to extent which is making the stanchion of a porous body frame. Moreover, the resin part was deposited after phase separation out of the solution, it was formed, and there was no improvement contribution in on the strength by extension orientation etc., the reinforcement as this kind of the whole low consistency porous body was weak, and, for that reason, that application was restricted. ** Although the detailed continuation hole was formed by the approach and it was strong in reinforcement, it was difficult to obtain the thing and the thing of a low consistency of the shape of a thick sheet. ** It was little continuation pore of the rate of the part which is equivalent to a cellular wall in a configuration similar to ** by the approach, even if it moreover made the pore diameter small, it was about at most 60-70 micrometers, and various things for which the pore diameter is made small were technically difficult although it inquired. ** Although the approach was continuously producible, even if the diameter of air bubbles was small, it was about at most 200 micrometers, and it was technically difficult to make the diameter of air bubbles small.

[0003] As mentioned above, although various approaches had been examined, in the foam which has an open cell, the diameter of air bubbles, the cellular configuration, and the foam consistency had the limit for which it comes from the process, respectively by the Prior art. The resin foam of a low consistency which serves as free passage air bubbles while it has the detailed cellular structure of 20 micrometers or less of diameters of air bubbles also especially in it and the cellular wall had moreover been made to remain substantially was what must have been attained.

[0004] The detailed air-bubbles resin foam which realizes lightweight-ization in the range on which reinforcement is not dropped for the purpose of reducing the amount of the thermoplastics used on the other hand is examined, and the attempt which makes the diameter of foam air bubbles small has been examined variously. For example, U.S. Pat. No. 4473665 and

Polymer Although the process of the resin foam of detailed air bubbles is indicated by Eng.Sc., 27, P485-492, and ANTEC.'91.P1406 - 1410 grade considering the purpose — each — a closed cell — and expansion ratio — 2 to 3 times (even if high about at most 10 times) as many foam as this — it is — the open cell of this invention — and the place clearly made into the aim differed from the resin foam of a low consistency (high twice foaming).

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EFFECT OF THE INVENTION

[Effect of the Invention] The thermoplastics foam of this invention is low consistency foam which formed continuation detailed air bubbles in homogeneity, and since the air bubbles moreover have the cellular wall substantially, it is excellent in reinforcement.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention makes a technical problem the low consistency resin foam which is an open cell with the conventional technique, having the detailed air bubbles of the polyhedron structure which is the so-called fundamental air-bubbles configuration of the resin foam which was not able to be attained, and having the cellular wall substantially.

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MEANS

[Means for Solving the Problem] In order to solve said technical problem, as a result of inquiring wholeheartedly about the detailed open cell [having had the cellular film substantially / are detailed air bubbles and] resin foam which was not examined at all conventionally, it came to complete this invention. namely, the thermoplastics foam of this invention — the diameter of air bubbles — 1-20 micrometers and cellular wall abundance — 80 - 100%, and the rate of an open cell — 90 - 100%, a consistency 20 - 100 kg/m³ it is — it is thermoplastics foam characterized by things.

[0007] Moreover, the manufacture approach of this invention is the manufacture approach of the thermoplastics foam characterized by foaming to the thermoplastics which made the resin particle whose particle diameter is 0.01-0.3 micrometers blend 0.05 to 5% of the weight by one 1.5 to 7 times the primary expansion ratio of this by multistage foaming. Hereafter, the contents are explained. The foam of this invention is foam which consists of air bubbles which have a cellular wall substantially, and the surface part ***** air-bubbles wall of polyhedron configuration air bubbles is foam characterized by air bubbles having free-passage-ized by having the deficit section represented in the hole through which matter, such as a gas and a liquid, may pass in a part of the cellular wall, a gash, etc., had.

[0008] The air bubbles and the cellular wall in this invention correspond to the definition of the cel and cel face which are specified with books "the activity of a cellular structure object and a porous material sake" (L. J.Gibson, M.F.Ashby work, a Masahisa Otsuka translation, Uchida Rokakuho Publishing Publishing office) respectively. A cel is the minute space of a polyhedron configuration with ** (edge) and a field (face), and, specifically, a cel face is a part defined by the field (face) surrounding a cel.

[0009] The diameter of air bubbles of the foam of this invention needs to be in the range of 1-20 micrometers. Here, the diameter of air bubbles of foam is the value which observed the cross section of foam and was calculated on the average based on ASTM D-3576 with the electron microscope photograph of an about 100 to 1000-time scale factor. When it uses as the description as detailed air bubbles, for example, a bulking agent for vacuum insulation, it is whenever [reduced pressure / of 10 to 1 or more mmHg], and in order to demonstrate the engine performance, it is necessary to be 20 micrometers or less. Moreover, since it becomes difficult to obtain the thing of a low consistency (it is difficult to make it quantity-double-foam), the thing of the less than 1-micrometer diameter of air bubbles is restricted. 2-15 micrometers of 3-10 micrometers of diameters of air bubbles are 4-8 micrometers still more preferably more preferably.

[0010] The cellular wall abundance of the foam of this invention needs to be in 80 - 100% of range. It specifically asks for the cellular wall abundance of foam with the following measuring methods. First, the existence of the deficit section of a cellular wall and its configuration select at least 20 or more air bubbles which can fully be observed from the enlargement (it observes for the scale factor for which at least 100 or more air bubbles are observed.) of the arbitration cross section of foam obtained by scanning electron microscope observation etc. Next, image-analysis equipment etc. is used, and it asks for that total (this value is set to A), after asking for each cross section of the selected air bubbles. About the air bubbles which furthermore have

the deficit section, it asks for that total (this value is set to B), after asking for that each aspect product (area when projecting a deficit part at right angles to a cross section so that it can measure on a photograph) of a deficit with image-analysis equipment etc. similarly. Here, with cellular wall abundance, the value (%) acquired by $\{1-(B/A)\} \times 100$ is adopted. A micro crack with observation difficult as that in which cellular wall abundance has area with a scanning electron microscope in 100% of thing here exists in a cellular wall, and is considered that air bubbles are open for free passage. Especially as for the foam characterized by the structure of having 80% or more of cellular wall of this invention, it is the greatest description that compressive strength is high in part since the cellular wall with which the deficit section was extended at the time of foaming of a certain thing exists in the cellular wall substantially. Since, as for less than 80% of thing, the compressive strength as foam tends to fall, cellular wall abundance is restricted. Cellular wall abundance is 98 - 100% of range still more preferably 95 to 100% more preferably 90 to 100%. The place which should be emphasized again here the cellular configuration of the foam of this invention The resin solid-state part which is the characteristic structure of the polyurethane system foam which has an open cell, and the porous body formed by the above-mentioned phase separation method is the arris part (the edge part which borders a cel face is meant as it defines as the above-mentioned reference book family register. cel edge:) of a polyhedron. The condensed structure is the point that the cellular configurations differ greatly, like a long and slender linear stanchion.

[0011] The rate of an open cell of the foam of this invention needs to be in 90 - 100% of range. When it uses as the description as an open cell, for example, a filler for vacuum insulation, it is necessary to be 90 - 100% because of prevention of a fall whenever [by compaction of vacuum reduced pressure time amount, and diffusion of the air from the closed cell section / reduced pressure]. This rate of an open cell is the value computed from the rate of a closed cell for which it asked based on ASTM D-2856. However, when it is foam in which the non-foamed layer on the front face of foam and the so-called skin were formed, the value in removal or the real busy condition after destroying in part is adopted for a skin. The approach of slicing and removing a skin part mechanically as an approach of removing or destroying a skin, the approach of forming a hole or a slot in a skin, the approach that make foam breaking easy to plasticize a skin with an additive and to carry out, or the approach heat concentrates with an additive at the time of foaming heating, and it is made to generate heat is chosen suitably, and it gets. The rate of an open cell is 99 - 100% still more preferably 97 to 100% more preferably 95 to 100%.

[0012] the foam consistency of the foam of this invention — 20 - 100 kg/m³ it is necessary to be . Consistencies are 20 kg/m³. For the thing of the following, since it is the inclination for foam reinforcement to become weak, it is restricted, and consistencies are 100 kg/m³. Since the inclination of the degree of lightweight-izing becomes small, what is exceeded is restricted. the foam consistency of this invention — desirable — 30 - 80 kg/m³ — more — desirable — 35 - 70 kg/m³ — further — desirable — 40 - 60 kg/m³ It is the range. This foam consistency is the value calculated based on JISK-6767.

[0013] As thermoplastics used for the foam of this invention Common well-known polycarbonate system resin, polymethacrylate system resin, polystyrene system resin, Polyphenylene ether system resin, polyarylate system resin, polysulfone system resin, Amorphous thermoplastics, such as polyether sulfone system resin and polyether imide system resin, Crystalline thermoplastics, such as polyethylene terephthalate system resin, polyphenylene sulfide system resin, polyamide system resin, a polypropylene resin, polyethylene system resin, and polyoxymethylene system resin, can use suitably in combination with the optimal foaming agent. Preferably, the so-called hard thermoplastics whose glass transition point of thermoplastics is beyond a room temperature is used from the holdout of the compressive strength in a room temperature. Also in it, especially the hard thermoplastics of amorphism nature has the description which detailed air-bubbles formation tends to carry out. They are polycarbonate system resin, polymethacrylate system resin, polystyrene system resin, and polyphenylene ether system resin still more preferably. They are the polycarbonate system resin which contains the so-called bisphenol A in a principal chain, and polymethacrylate system resin which contains methyl methacrylate in a principal chain especially preferably.

[0014] Although it can use independently, these resin may be blended and used in order to improve the resin melt viscosity in the heating condition at the time of foaming, and the holdout of a foaming agent. Additives, such as well-known lubricant, a thermostabilizer, and an ultraviolet ray absorbent, may be added and used in the range which does not change fizz to 1 pan remarkably if needed. Next, the manufacture approach of this invention is explained.

[0015] In order to manufacture the foam of this invention, it is important to combine the formula which makes homogeneity generate remarkable detailed air bubbles compared with usual foam, and the formula which makes the detailed air bubbles made to generate open-cell-ize in early stages of foaming. The method of sinking in and heating the high-pressure carbon dioxide gas in a gaseous-phase condition, a liquid phase condition, and a supercritical condition, nitrogen gas, oxygen gas, air, etc. to the thermoplastics which put in the physical foaming agent into the high pressure vessel as a formula which generates detailed air bubbles to homogeneity in the so-called sinking-in foaming into which resin was infiltrated, and which carries out a late-coming bubble under high pressure in consideration of temperature and time amount, and making it generate detailed air bubbles can take. In extrusion foaming, high-pressure carbon dioxide gas, nitrogen gas, oxygen gas, air, etc. are poured into the resin fused within the extruder, and the approach of adjusting resin viscosity more highly and carrying out open aggressiveness foaming at a dice outlet can take. Moreover, as a formula which makes the detailed air bubbles made to generate open-cell-ize, the approach of promoting foam breaking (a cellular wall being open cell-ization by the defective-part formation by destruction a part) can take by sinking-in foaming by investigating the relation of the foaming temperature and the expansion ratio which are the foaming conditions after sinking in, and heating at the temperature which shows the peak of the expansion ratio of resin. However, the approach for which it was suitable especially as an approach of obtaining the foam of this invention is the manufacture approach of this invention shown below. Hereafter, the contents are explained.

[0016] The manufacture approach of this invention is the manufacture approach of the thermoplastics foam characterized by foaming to the thermoplastics which made the resin particle whose particle diameter is 0.01-0.3 micrometers blend 0.05 to 5% of the weight by one 1.5 to 7 times the primary expansion ratio of this by multistage foaming. It describes from the formula which makes detailed air bubbles generate first. adding non-subtlety particles, such as talc, a silica, and a magnesium oxide, and using it as a foaming nucleating agent at the time of foaming by extrusion foaming, conventionally, inquires — having had (for example, J.Appl.Polym.Sci., 28, 1983 grades) — at most, even if the diameter of air bubbles was small, it was about 200 micrometers. The detailed air-bubbles resin foam which used HIPS (high-impact-polystyrene resin) for reference (ANTEC.'92.P1078-1081, ANTEC.'93.P1828-1831) in order to make the diameter of air bubbles small furthermore is indicated. The resin which blended the butadiene system rubber particle in polystyrene resin is known in order to improve the shock resistance of polystyrene generally. Although magnitude, its amount of blends, etc. of a rubber particle were examined variously, for shock-proof amelioration, the diameter of a rubber particle was made suitable [that whose amount of blends is 10 - 30 % of the weight], and, as for these, came by about 1-2.5 micrometers. It is presumed that that serves as a foaming nucleus since a micro void occurs in the rubber particle of the diameter of an average of 2 micrometer with the thermal stress generated by this reference when the coefficients of thermal expansion of a polybutadiene-resin part and polystyrene resin differ in HIPS. A particle consistency and a cellular consistency (a cellular consistency is surveyed from the cross-section microphotography of foam) the number of air bubbles per foam unit volume — an individual / cm³, so that expansion ratio is so high that it expresses in a unit and the diameter of air bubbles is small — more — a cellular consistency — high — becoming — 108 -1010 piece/cm³ in the range, it is proportional — Moreover, since some whose diameter of a polybutadiene particle is 2 micrometers have the effectiveness as a foaming nucleus, what is 0.025 micrometers is too small and the effectiveness does not exist, although it is not in **, it is also indicated that the diameter of criticality of the diameter of a particle which contributes effectively exists. However, although there is no publication about expansion ratio, it is presumed that it is low expansion ratio compared with this invention. for making expansion ratio high in order to be in level (it is

the range of 3 1010–1013 pieces/cm when it says by the cellular consistency) still higher than the cellular consistency indicated by this reference by this invention and to make it a low consistency moreover, it is necessary to improve holdout of the foaming agent in air bubbles — in addition, the thing of making a cellular wall tear and open-cell-ize done for phase conflict must be made to attain By the system which blended 2 micrometers of diameters of a particle of the publication proved by reference, it is impossible. That is, if the particle which exists in a cellular wall is too large, before a cellular wall will reach need expansion ratio, foam breaking is carried out, if a particle is too small, it cannot become an effective foaming nucleus, or a cellular wall will not be made to generate a micro crack, but extent of the formation of free passage air bubbles will become low. However, a certain amount of difference may generate the behavior in the cellular wall of this particle with the rate of the deformation which followed in footsteps of the cellular wall by plasticization extent of the particle by the foaming agent, or the change rate of the viscoelasticity in foaming temperature. While advancing this invention based on such an operation result, the conditions whose detailed foaming is enabled were found out in a different field from what was examined by the conventional shock-proof amelioration about the diameter of a rubber particle, and its amount of blends. It is thought that this effectiveness has contributed to micro crack generation of a cellular wall to think because for resin and a particle interface to serve as a foaming nucleus in early stages of foaming, and also for this interface consider as an open cell finally. Specifically, detailed foaming was attained by blending a resin particle with a particle diameter of 0.01–0.3 micrometers 0.05 to 5% of the weight to thermoplastics. A resin particle here may be a globular form particle by which a polymerization is carried out by the general well-known emulsion polymerization, the seed polymerization, the distributed polymerization, a suspension-polymerization method, etc., and may be a particle which has a core shell mold and multilayer structure in consideration of particle dispersibility, the foaming agent dispersibility after sinking in, etc. Preferably, a multilayer-structure acrylic (polymethylmethacrylate) rubber system particle, a styrene-butadiene system rubber particle, an acrylonitrile-styrene-butadiene system particle, a silicon system particle, a polystyrene particle, a polymethylmethacrylate particle, etc. are used. It cannot become a foaming nucleus, and if too small, if too large, open cell-ization will take place in early stages, and since it is in the inclination for expansion ratio to become low, the diameter of a particle is restricted. The range of 0.05–0.2 micrometers of diameters of a particle is 0.07–0.15 micrometers still more preferably preferably. The diameter of a particle here adopts the value which averaged the electron microscope etc. from observation and was calculated. if there are still too few amounts of blends of a particle — a foaming nuclear number — being few (the diameter of air bubbles becoming large) — moreover, if many [too], open cell-ization will take place in early stages, and since it is in the inclination for expansion ratio to become low, it is restricted. The amount of blends is 0.07 – 0.5 % of the weight still more preferably 0.05 to 1% of the weight preferably. A well-known compatibilizer etc. may be used together if needed [of improving dispersibility and the adhesive property of an interface].

[0017] Although it furthermore adds and is crystallinity originally [, such as polycarbonate resin and polyethylene terephthalate resin,] as this formula, when making it foam, by the resin which can take amorphous state by the quenching processing at the time of processing etc., very detailed air bubbles can be formed by making the microcrystal generate. For example, the processing which can form a microcrystal is suitably chosen at the time of foaming agent sinking in with plasticizing capacity, such as heat treatment and solvent processing before foaming agent sinking in, and/or carbon dioxide gas. What was immersed in the aliphatic series system hydrocarbon system partially aromatic solvent included a 15 capacity % grade in the acetone, specifically carried out solvent processing of the polycarbonate resin, sank in and foamed to carbon dioxide gas after that serves as foam which has very detailed air bubbles. In addition to solvent processing, by having carried out carbon-dioxide-gas sinking in, a microcrystal (less than 5% has the desirable degree of crystallinity by temperature up conditions by DSC:10-degree-C/) generates to homogeneity in polycarbonate resin, it serves as a foaming nucleus, and this is considered to be the effectiveness by the cellular nuclear number having increased remarkably. Moreover, it is desirable to adjust degree of crystallinity to 0.1% or more in that the effectiveness

of having made the microcrystal which can serve as a foaming nucleus generating is demonstrated.

[0018] Next, the detailed air bubbles made to generate are described about the formula made to open-cell-ize. As an approach to which the resin adjusted like the above is made to foam in the manufacture approach of this invention Although the so-called extrusion foaming to which release ** and it is made to foam can be suitably chosen after pressing a foaming agent fit in the resin which fused the physical foaming agent within the so-called sinking-in foaming into which resin is infiltrated, and an extruder under high pressure and mixing to homogeneity In any case, when foaming and foam breaking (a cellular wall is open cell-ization by the deficit section formation by destruction a part) cannot be satisfied with coincidence of the physical properties of the foam of this invention at the time of one step of usual foaming, it is very effective to perform multistage foaming of sinking in and foaming to a physical foaming agent again at the obtained foam. this holding down the first step of foaming to one 1.5 to 7 times the expansion ratio of this for the purpose of forming many foaming nuclei, and raising further the mind bubble pressure inside the air bubbles formed in the foam formed by primary foaming after the second step of foaming — it is — the high twice of expansion ratio — it is a formula aiming at-izing and foam breaking. It cannot be overemphasized that the method of foaming multistage [three or more steps of] for performing sinking in and foaming further can be taken if needed. that, as for what there is an inclination which air bubbles generate [primary expansion ratio] to an ununiformity by less than 1.5 times, and exceeds 7 times, the diameter of air bubbles increases by coalescence of air bubbles in the phase, and foam breaking — foaming quantity twice — since there is an inclination for-izing to become difficult, it is restricted. It is 2.5 to 5 times the primary expansion ratio of this more preferably two to 6 times. The amount of sinking in of the physical foaming agent used by primary sinking in can be suitably chosen in the range of 6 – 40 weight section, taking into consideration a foam consistency, i.e., expansion ratio. desirable — 8 – 30 weight section — it is 10 – 24 weight section more preferably.

[0019] The solvent system foaming agent, organic, and the inorganic system gas foaming agent which are used for general well-known foam as a physical foaming agent used by this invention are chosen suitably, and it gets. Specifically Normal butane, an isobutane, a normal pentane, a cyclopentane, Aromatic hydrocarbon, such as aliphatic hydrocarbon, such as normal hexane, benzene, toluene, and a xylene, Ketone system hydrocarbons, such as an acetone and a methyl ethyl ketone, a methanol, Alcoholic system hydrocarbons, such as ethanol, dihydrodifluoromethane, pentafluoro ethane, It is inorganic gas, such as fluorine-containing hydrocarbons, such as 1, 1, 2, and 2-tetrafluoro ethane, 1, 1 and 1, 2-tetrafluoro ethane, 1 and 1, 1-trifluoro ethane, 1, and 1-difluoroethane, 1, and 2-difluoroethane, carbon dioxide gas, and nitrogen gas, oxygen gas, etc. Especially in order to make it small making [many / as possible] the cellular nuclear number per foam unit volume of air bubbles, i.e., the diameter in fixed expansion ratio, carbon dioxide gas is desirable. Moreover, other physical foaming agents may be used together or ***** (ed) to carbon dioxide gas for the purpose which increases the cellular nuclear number at the time of foaming. The amount of sinking in of a foaming agent is usually 3 – 25 weight ***** , although it is suitably chosen with the physical foaming agent to be used and being got. desirable — 5 – 20 weight section — it is 7 – 15 weight section more preferably.

[0020] As a physical foaming agent which sinks into foaming after secondary again, in consideration of primary expansion ratio, plasticization extent by sinking in, the foaming temperature after secondary, expansion ratio, the rate of open-cell-izing, etc., it is suitably chosen from the below-mentioned physical foaming agents, and gets. if it is not made to foam, carrying out foam breaking of the cellular wall of the closed cell formed by foaming in the preceding paragraph at the time of foaming after secondary, it is necessary to make gas pressure in air bubbles into height, and while the amount of sinking in of a foaming agent takes into consideration a foam consistency, i.e., expansion ratio, in the range which fulfills the condition, for a 7 ** reason, it can choose suitably in the range of 6 – 40 weight section. desirable — 8 – 30 weight section — it is 10 – 24 weight section more preferably.

[0021] The physical foaming agent which can be used by this invention is introduced in high

pressure vessels, such as an autoclave into which a well-known approach, for example, the bead of thermoplastics, powder, a pellet, a sheet-like object, etc. were put, and it sinks in under high-pressure conditions. Sinking-in conditions and the amount of sinking in are suitably chosen in consideration of the expansion ratio and foaming temperature which are needed, and it deals in them. Moreover, in the case of extrusion foaming, a sinking-in condition can be chosen as the fused resin for a physical foaming agent by the distributed mixing **** technique. Moreover, when making the thing of the shape of a bead of the thermoplastics in which it is produced by the suspension polymerization and deals foam, a physical foaming agent can be added in the second half of the suspension polymerization, and an expandable bead can also be obtained.

[0022] As a heating means at the time of foaming, hot blast heating which is a well-known approach, heating oil heating, far infrared heating, steam heating also including primary foaming and subsequent multistage foaming, etc. are chosen suitably. When especially the resin with comparatively high steam permeability, such as styrene resin and polycarbonate resin, carries out steam heating, using the property effectively, quantity twice foam is obtained.

[0023] It is also the description that the foam of this invention is obtained in a process with the simple thing of the configuration of arbitration to the foam of particle shape which is represented by styrene system bead foam, and the foam of a sheet configuration.

[Translation done.]

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

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3.In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, this invention is explained to a detail using an example.

[0025]

[Example 1] By the approach given in JP,3-68627,A, melting extrusion was performed for the pellet of the polycarbonate resin (weight average molecular weight 56,000) manufactured from diphenyl carbonate and 2 and 2-screw (4-hydroxyphenyl) propane at 320 degrees C of cylinder temperatures using the extruder, and the sheet with a thickness of 1mm was created.

[0026] A 20x30mm sample is started from this sheet, and it puts into a small autoclave, and is a liquefied carbon dioxide at 5 degrees C 40kg/cm² It pressed fit and was left for 24 hours so that it might become. Then, when ** was released and the weight of a sample was measured, the 13.5 weight sections and carbon dioxide gas sank in to sample weight. When it was immersed in the oil bath with a temperature of 150 degrees C for 30 seconds, and this sinking-in sample was heated to it and made to foam to it primarily, foam 4.8 times the scale factor of this was obtained.

[0027] this primary foaming article — again — a small autoclave — putting in — the same — carbon dioxide gas — 60kg/cm² up to — it pressed fit and was left at 23 degrees C for 24 hours. Then, it was left at 23 degrees C to the condition that release ** and 15 weight sections carbon dioxide gas sinks in to sample weight. When it was immersed in the oil bath with a temperature of 190 degrees C for 15 seconds, and this sinking-in sample was heated to it and made it to carry out post expansion, it is consistency 57 kg/m³. Foam of 7 micrometers of diameters of air bubbles was obtained.

[0028] The cellular wall abundance which searched for the 1000 times as many electron micrograph as this foam cross section with image-processing analysis equipment (SPICCA-II by Nippon Avionics [Co., Ltd.] Co., Ltd. is used) was 98%, and the rate of an open cell of foam (the sample was quadrisected and measured in order to remove the effect of a skin) was 99%.

Therefore, although almost all air bubbles were open cells, it turned out that it has the cellular wall substantially.

[0029]

[Examples 2-5] Examples 2-4 manufactured foam on the conditions which an example 5 is the same approach as an example 1 using the polycarbonate resin (Teijin Formation bread-making light K-1300) of weight average molecular weight 30,000, and show the same resin as an example 1 in Table 1. The physical properties of the obtained foam are shown in Table 1.

[0030]

[Example 6] After carrying out the dryblend of the acrylic particle (acrylic rubber SRS by Asahi Chemical Industry Co., Ltd.: particle diameter of 0.1 micrometers) to polymethylmethacrylate resin (DERUPETTOby Asahi Chemical Industry Co., Ltd. 980N) at 0.1% of the weight of a rate, with the geared type said direction twin screw extruder, water-cooled desiccation was carried out after extrusion at 250 degrees C, and the melting blend pellet was obtained. Press forming of this blend pellet was carried out, and the sheet with a thickness of 1mm was obtained. When the 20x30mm sample was started from this sheet, it put into the small autoclave and 80 degrees C sank in over 60 hours by HFC134a (1, 1, 1, 2-tetrafluoro ethane) of a liquid phase condition, the amount of sinking in was 25 weight sections. It was immersed in the 150-degree C silicon oil bath for 30 seconds, and foamed to this sinking-in sample, and the primary foaming article 6.5

times the expansion ratio of this was obtained. When this sample was again put into the autoclave and 30 degrees C sank in over 48 hours by HFC134a of a gaseous-phase condition, the amount of sinking in was 35 weight sections. This sinking-in sample was immersed in the 150-degree C silicon oil bath for 30 seconds, and the post expansion object was acquired. the diameter of air bubbles of this foam — 3 micrometers and cellular wall abundance — 95% and the rate of an open cell — 95% and a consistency — 70kg/m3 it was .

[0031]

[Example 7] The 30x20mm sample was started from the same sheet as an example 1, it was immersed in the mixed solution of acetone:n pentane =20:80 (capacity factor) at the room temperature for 24 hours, and the solvent processing sheet containing 10 weight sections partially aromatic solvent was obtained. this sheet — a small autoclave — putting in — carbon dioxide gas — 40kg/cm2 up to — it pressed fit and was left at 5 degrees C for 24 hours. Then, when ** was released and the weight of a sample was measured, 20 weight sections, carbon dioxide gas, and a solvent sank in to sample weight. the part which was not observed with the sheet before sinking in in a part of this sinking-in sample although it was 3% or less when that degree of crystallinity was measured in DSC — crystallization was seen.

[0032] When it was immersed in the oil bath with a temperature of 150 degrees C for 30 seconds, and this sinking-in sample was heated to it and made to foam to it primarily, foam 3.0 times the expansion ratio of this was obtained. this primary foaming article — again — a small autoclave — putting in — the same — carbon dioxide gas — 40kg/cm2 up to — it pressed fit and was left at the room temperature for 24 hours. ***** was released, it aged at the room temperature, and 13 weight sections carbon dioxide gas changed into the condition of sinking in, to sample weight.

[0033] When it is immersed in an oil bath with a temperature of 190 degrees C for 15 seconds, and this sinking-in sample is heated to it and made it to carry out post expansion, the diameter of air bubbles is [99% and the rate of an open cell of 5 micrometers and cellular wall abundance] 90%, and consistencies are 50 kg/m3. Foam was obtained. Compared with an example 1, a foaming nucleus increases this foam by solvent processing, and the diameter of air bubbles is considered to have become small.

[0034]

[The example 1 of a comparison] With the oil bath with a temperature of 190 degrees C, it was immersed for 30 seconds, the primary sinking-in sample obtained on the same conditions as an example 1 using the same resin as an example 1 was heated, and foam was obtained. the diameter of air bubbles of the obtained foam — 9 micrometers and cellular wall abundance — 99% and a consistency — 45 kg/m3 it was — although — the rate of an open cell was a low value compared with 57% and an example.

[0035]

[The example 2 of a comparison] The mixed solvent (70:30 capacity %) of 10 weight sections, and a dioxane/cyclohexane was heated at 60 degrees C on ***** which becomes a depth of about 1cm about 90 weight sections at a metal cylinder container with a diameter of 50cm, and an oil bath, and the same polycarbonate resin as an example 5 was dissolved in homogeneity. It was rapidly immersed in the dry ice bus, this container was quenched below to solidification temperature, and resin porosity intermediate field were obtained. While the vesicular structure had been made to hold this intermediate field using a freeze dryer, the solvent was removed, and the resin porous body was obtained. the diameter of air bubbles of this resin porous body (path of the part equivalent to the diameter of air bubbles in foam) — 5 micrometers — it is — cellular wall abundance — 0% — it is — the rate of an open cell — 100% and a consistency — 115 kg/m3 it was . This resin porous body did not have a cellular wall substantially so that cellular wall abundance might show, and that compressive strength was remarkably low compared with the foam of this invention.

[0036]

[Table 1]

(単位)	実 施 例							比 較 例	
	1	2	3	4	5	6	7	1	2
熱可塑性樹脂	PC	PC	PC	PC	PC	PMMA	PC	PC	PC
一次含浸									
・発泡剤	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	134 a	CO ₂	CO ₂	相分離法
・含浸温度 (°C)	5	5	5	5	5	80	5	5	
・含浸圧力 (kg/m ²)	40	40	40	40	40	24	40	40	
・含浸時間 (時間)	24	24	24	24	24	60	24	24	
・含浸量 (重量部)	13.5	11.5	10.5	12.5	13.0	25	20	13.5	
一次発泡									
・加熱温度 (°C)	150	150	155	155	150	150	150	190	
・加熱時間 (時間)	30	30	30	30	30	30	30	30	
・発泡倍率 (倍)	4.8	3.4	5.5	5.0	3.3	6.5	3.0	26.0	
二次含浸条件									
・発泡剤	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	134 a	CO ₂		
・含浸温度 (°C)	23	5	5	23	23	30	5		
・含浸圧力 (kg/m ²)	60	40	40	60	60	48	40		
・含浸時間 (時間)	24	24	24	24	24	24			
・含浸量 (重量部)	15.0	18.0	8.5	12.5	13.0	34.5	13.0	—	—
二次発泡									
・加熱温度 (°C)	190	190	190	190	185	150	190		
・加熱時間 (時間)	15	15	10	20	15	30	15		
発泡体物性									
・気泡径 (μm)	7	8	15	10	20	3	4	9	5
・気泡壁存在率 (%)	98	98	90	98	95	95	99	99	0
・連続気泡率 (%)	99	99	99	100	100	95	96	57	100
・密度 (kg/m ³)	57	40	95	31	24	70	50	45	115

[Translation done.]